A Complete Method for Environmental Samples by Simultaneous Axially Viewed ICP-OES following US EPA Guidelines

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Authors

Scott Bridger

Mike Knowles

Introduction

With the growing demand for elemental analysis of environmental samples and the financial pressures being applied to the modern laboratory, development of a universal method for a wide range of sample types is needed. The Agilent Vista ICP-OES, with simultaneous measurement of the entire elemental spectrum facilitates such universal methods.

The Vista instrument has a number of distinct advantages over similar ICP-OES systems. Firstly, the VistaChip is the only single Charge Coupled Device (CCD) that allows full coverage of the spectrum from 165-785nm, with a pixel processing speed of 1 MHz and exceptional anti-blooming properties. These features allow both trace level analytes and major analytes to be determined in the same measurement. Secondly, the RF robustness of the Vista ICP-OES permits the analysis of difficult samples, up to 5% total dissolved solids, using an axially viewed plasma. Finally, the Cooled Cone Interface (CCI) of the axially viewed Vista eliminates the cooler tail of the plasma, reducing Easily Ionizable Element (EIE) interferences and maximizing linear dynamic range. The CCI consists of a cooled nickel cone with a large orifice at its tip, positioned to view the optimum region of the axial plasma.

The greatest challenge in creating one method for all analytes is achieving the dynamic range coverage from low parts-per-billion for the toxic elements to high parts-per-million for the Group I and II elements. With the Vista this is further facilitated by software features such as MultiCal, which allows multiple wavelengths to be used simultaneously for the same element to provide complete coverage of the linear dynamic range. MultiCal allows the user to assign the valid linear dynamic range to each wavelength used.

The user enters the allowable minimum and maximum concentration for each wavelength so that the software can then automatically assign sample results to the appropriate wavelengths. The software preferences can then be set to only display concentrations that fall within this valid range. By combining multiple wavelengths

in this way, the Vista manages the full dynamic range capabilities of the VistaChip from sub ppb levels to low percentage levels. Another software capability, Adaptive Integration, automatically assigns the integration time for each wavelength in real time, to achieve the optimum signal to noise ratio. For example, a high level signal for a matrix element such as Na, might be assigned multiple, shorter integration times, ensuring that this signal is within range and also improving precision statistics through the multiple readings. Simultaneously, a low level analyte of interest such as Pb, might be assigned the full integration time requested by the user, thereby ensuring optimum signal to noise ratio and detection limits. With Adaptive Integration these two measurement sequences can be conducted simultaneously, whereas conventional systems have to sequence these different integration times with the resultant longer analysis times.

As a result the Vista simultaneous ICP-OES is able to measure all required elements in a single environmental analysis using axial viewing. Alternative techniques such as dual viewed plasmas, require the samples to be analyzed first with axial viewing and then with radial viewing to accommodate the linear dynamic range of the target elements.

The use of the dual viewed plasma will therefore significantly lengthen the analysis time. Direct analysis using the Vista provides a significant saving, in analysis time and running costs particularly argon consumption.

In this work, the steps to develop a universal method for the analysis of waters and wastewaters are reviewed. As a measure of success, the US EPA guidelines for data quality control for these sample types have been used. The primary guiding documents for this analysis type from the US EPA are CLP ILMO 4.0 [1] and ILM05.0 [2] and Methods 200.7 [3] and 6010B [4]. These protocols describe strict rules for establishing calibration validity, linear dynamic range and management of interferences, thus ensuring data quality. It should be noted that these protocols are 'living documents' which undergo a process of continual development. For example, ILM04.0 is currently undergoing revision to ILM05.0 [2].

In this work, terminology from the ILM04.0 and ILM05.0 documentation is used, however a table of analysis sequence is offered which translates the protocols into the language of the different source documents. The method developed here has been applied to typical water and waste water samples.

The data Quality Control Protocols (QCP) provided as standard with the Vista software have been used in this work to meet the US EPA data validation guidelines. The Vista QCP package consists of a series of automated tests designed around these guidelines however these are adaptable to any other protocol by the use of a simple programmable language and user definable tests. The QCP software allows the user to specify the corrective action that will occur on a QCP solution test failure with options such as Recalibrate and Repeat With Samples, Flag and Continue and Stop. With the addition of the Varian autosampler and diluter which provides on-line over range dilution, the Vista ICP requires minimal supervision during the analysis, resulting in further resource savings.

Instrument Set up

An Agilent Vista simultaneous ICP spectrometer with an axially viewed plasma was used for this analysis. The instrument was fitted with the mass flow controller option on the nebulizer gas and with the 3 channel peristaltic pump option. The operating conditions for the instrument were obtained by following the criteria documented in the SOW (Statement of Works) for Methods 200.7, 6010B and ILM 04.0 and 05.0. Parameters were then optimised to obtain the best performance from the ICP-OES system.

The final instrument operating conditions are given in Table 1. Particular attention was paid to the Method Detection Limits (MDL) in the final acceptance of the operating conditions. All test solutions and calibrants were from Inorganic Ventures (Lakewood, NJ, USA) using their US EPA 200.7 kit.

Table 1. Instrument Operating Conditions

Power	1.40 kW
Plasma gas flow	15.0 L/min
Auxiliary gas flow	0.75 L/min
Nebuliser type	SeaSpray Glass Concentric (Glass Expansion, Melbourne Australia).
Nebuliser gas flow	0.75 L/min
Pump speed	15 rpm
Sample tubing	White/White
Internal standard tubing	Orange/White
Sample delay	40 sec
Rinse time	40 sec between each sample
Replicate time	30 sec
Stabilisation time	10 sec
Replicates	2
Background correction	Left and right off peak
Autosampler	Agilent SPS-5 5

An ionization buffer consisting of up to 1% $CsCl_2$ (Merck, Germany) with 10 mg/L yttrium (EM Science Gibbstown, NJ, USA) as internal standard and 0.1% Triton X100 (LabChem, Auburn, Australia), was connected to the sample flow via a post-pump T-piece (1/16" diameter, Cole Palmer, Illinois, USA part number 6365-77). The $CsCl_2$ ionization buffer is used to suppress the ionization effects of EIE, resulting in improved calibration linearity. This approach has been approved by the US EPA in one region of the USA [5], and so it is expected that written approval in other regions for this approach should be reasonably obtained. The yttrium is added as internal standard and the addition of the Triton X100 provides improved spraychamber wetting [6] for optimum precision.

Results - Method Detection Limits (MDL) and Linear Dynamic Range (LDR)

Having optimized the instrument conditions the MDL's were measured in accordance with USEPA documentation for a range of replicate read times. The definitions of Instrument Detection Limits (IDL) versus Method Detection Limits (MDL) and indeed Contract Required Detection Limit (CRDL) in the EPA literature are often confused.

In some documents the IDL is taken to mean an instrument detection limit achieved under manufacturer's recommended conditions in a dilute acid matrix. In this work the definition of Instrument Detection Limit (IDL) was taken from Exhibit E-10 of the ILM 04.0 Statement of Work [1].

To paraphrase this definition "the IDL shall be determined as 3xStandard Deviation of seven consecutive measurements of a standard solution at a concentration of 3-5 x the manufacturer's suggested IDL on three non-consecutive days". In other documentation this technique is described as an MDL [4] -this is probably a more appropriate designation in distinguishing between the ultimate IDL obtainable at any time and the more representative MDL obtained over several days. The results of determination of the IDLs by the ILM0.40/05.0 method are shown in the Table 2. These detection limits were obtained by averaging a pool of results from four separate Vista instruments around the world [8]. Due to the inherent uncertainty in detection limit measurements the results have then been rounded to only one significant figure. The IDLs obtained in this way must meet the levels specified in Exhibit C of the ILM04.0/05.0 Exhibit C is the table of Contract Required Detection Limits (CRDL). Table 2 shows that the CRDLs are met with a replicate read time of 30 sec.

Table 2.

Element	CRDL ILM 04.0 [1] (ug/L)	CRDL ILM 05.0 [2] (ug/L)	IDL 60sec (µg/L)	IDL 30sec (µg/L)
Ag 328.068	10	5	0.5	0.7
Al 236.705	200	200	10	12
Al 308.215	200	200	1	1
As 188.980	10	5	2	3
Ba 233.527	200	20	0.2	1
Ba 585.367	200	20	0.5	3
Be 234.861	5	1	0.1	0.2
Be 249.473	5	1	1	2
Be 313.042	5	1	0.2	0.5
Ca 370.602	5000	5000	200	300
Ca 315.887	5000	5000	1	2
Cd 226.502	5	2	0.2	0.3
Co 228.615	50	5	0.3	0.6
Co 238.892	50	5	1	2
Cr 267.716	10	5	0.2	0.5
Cu 327.395	25	5	0.6	1
Fe 259.940	100	100	0.5	1
Fe 258.588	100	100	1	2
K 404.721	5000	5000	1000	2000
K 766.491	5000	5000	2	2
Mg 383.829	5000	5000	5	10
Mn 257.610	15	10	0.2	0.5
Mn 261.020	15	10	3	5
Na 330.237	5000	5000	70	300
Na 589.592	5000	5000	1	2
Ni 231.604	40	20	1	1
Pb 220.353	3	3	2	2
Sb 206.834	60	5	2	4
Se 196.026	5	5	3	4
Tl 190.794	10	5	2	3
V 292.401	50	10	0.5	1
Zn 206.20	20	10	0.5	0.6

* IDLs calculated over 3 non-consecutive days [1,8] and rounded to one significant figure

Linear Range Analysis (LRA)

According to ILM04.0/05.0, a linear range verification check standard must be analyzed and reported quarterly for each analyte. The concentrations of the analytes in the LRA standard define the upper limit of the ICP linear range beyond which results cannot be reported without dilution. The analytes in the LRA standard must be recovered to within ± 5% of their true values. It is in the interest of every laboratory therefore to formulate an LRA standard with acceptable recoveries at the highest possible concentrations for each element. In most cases, high concentrations are generally only expected for the major elements such as Fe, K, Ca, Na, Mg and possibly Al. Table 3 shows the results of the LRA obtained during this work. It should be noted that silver is particularly prone to precipitation from solution at high concentrations. The US EPA recommends adding an excess of hydrochloric acid to avoid this precipitation and limiting the maximum concentration of Ag to 2 mg/L in solution [1]. In this work it was found that Ag calibrations became curved at concentrations of 5 mg/L or higher, and so the Ag calibration range was restricted to 2 mg/L to obtain good linearity.

Using the Vista's MultiCal feature a second wavelength was added for the elements Fe, K, Na, Ca and Al as shown in Table 3.

During the analysis Vista automatically assigns sample results to the wavelength that has the appropriate user defined linear dynamic range (LDR). In the same way, the automatic data QCP tests and actions are only applied to those wavelengths for which the results fall within the specified LDR. For example, referring to Table 3, an iron result of 70 ppm would be automatically measured and QC-assessed against the 258.258 nm wavelength, not the 259.940 nm wavelength.

The LRA results in Table 3 include some later work in which useful alternate wavelengths were found for a number of elements. These alternate wavelengths are indicated in the table. Note that these wavelengths were found to be suitable for analysis from the detection limit to the LDR limit, but with the MultiCal feature it is possible to restrict the lower concentration limit of the calibration to a non-zero value as mentioned above for iron 259.940 nm.

It should also be noted that the on-line overrange dilution capability of the Vista can be used in conjunction with MultiCal to ensure complete compliance with the US EPA regulations with unattended operation.

Table 3. Linear Range Analysis for Recommended Wavelengths for the 22 US EPA Elements. Note That Some Additional Elements Studied In This Work Have Been Included Such As Boron.

Element	Curve type	Minimum concentration per line (mg/L)	Maximum concentration per line (mg/L)
Ag 328.068	Linear	0	2
Al 236.705	Linear	200	2000
Al 308.215	Linear	0	200
As 188.980	Linear	0	100
B 249.772	Linear	0	100
Ba 585.367	Linear	0	100
Be 313.042 (alternates 234.861 and 249.473 nm)	Linear	0	10
Ca 370.602	Linear	0	2000
Ca 315.887	Linear	0	200
Cd 226.502	Linear	0	10
Co 228.615 (alternate 238.892 nm)	Linear	0	100
Cr 267.716	Linear	0	100
Cu 327.395	Linear	0	100
Fe 259.940	Linear	100	2000
Fe 258.258 (alternate 258.588)	Linear	0	100
K 404.721 (alternate 693.876 nm)	Linear	100	2000
K 766.491	Linear	0	100
Mg 383.829	Linear	0	2000
Mn 261.020	Linear	0	1000
Na 330.237	Linear	50	2000
Na 589.592	Linear	0	100
Ni 231.604	Linear	0	100
Pb 220.353	Linear	0	50
Pb 283.305	Linear	0	100
Sb 206.834	Linear	0	10
Se 196.026	Linear	0	10
Tl 190.794	Linear	0	10
V 311.837 (alternate 292.401 nm)	Linear	0	100
Zn 334.502	Linear	0	100

The recommended background correction points for each wavelength are shown in Table 4.

Table 4. Background Correction Points for Recommended Wavelengths (n.u. Indicates "not used")

Element	Wavelength (nm)	BC point left (nm)	BC point right (nm)
Ag	328.068	0.020	n.u.
Al	308.215	0.020	n.u.
Al	236.705	0.020	n.u.
As	188.890	0.020	n.u.
Ba	585.367	0.062	n.u.
Be	234.861	0.018	n.u.
Be	249.473	n.u.	0.020
Ca	370.602	0.024	n.u.
Ca	315.887	0.024	n.u.
Cd	226.502	0.020	n.u.
Co	238.892	0.020	n.u.
Co	228.615	0.016	n.u.
Cr	267.716	0.020	n.u.
Cu	327.395	0.020	n.u.
Fe	259.940	0.020	n.u.
Fe	258.588	0.020	n.u.
K	766.491	0.113	n.u.
K	693.876	n.u.	0.087
K	404.721	0.020	n.u.
Mg	383.829	0.036	n.u.
Mn	261.02	0.020	n.u.
Na	589.592	0.080	n.u.
Na	330.237	0.028	n.u.
Ni	231.604	0.020	n.u.
Pb	283.305	0.020	n.u.
Pb	220.353	0.012	n.u.
Sb	206.834	0.020	n.u.
Se	196.026	0.012	n.u.
Tl	190.794	0.011	n.u.
V	292.401	0.024	n.u.
Zn	334.502	0.022	n.u.

Initial and Continuing Calibration Verification (ICV, CCV) and Analytical Samples

The QC tests outlined in the various SOWs are designed to ensure the accuracy and precision of the results produced. The results shown in Figures 1-4 are in accordance with the specification detailed in CLP ILM 04.0/ILM 05.0 SOW [1]. The Initial Calibration Verification (ICV) test is conducted immediately after instrument calibration. The ICV solution is a check standard either obtained from the EPA or from a secondary source, other than that used to prepare the calibration standards. All analytes in the ICV must be recovered within ±10% of the certified value.

The Continuing Calibration Verification test is used to ensure the validity of the calibration throughout the analysis run and is carried out at a frequency of 10% (every 10 analytical samples) or every 2 hours, whichever is more frequent. The definition of an analytical sample is best given by exception - the Glossary of ILM0.40 defines an Analytical Sample as "any solution ... on which analysis is performed excluding instrument calibration, ICV, ICB, CCV and CCB". This means that if a sample is automatically diluted, the frequency counter must be incremented by the number of dilutions - this is done automatically by the Vista software.

The CCV is also measured at the beginning (but not before the ICV) and end of the analysis run. The CCV must be recovered between 90% and 110% (ILM04.0/05.0) of the true value. Method 200.7 features an Instrument Performance Check (IPC) solution and requires that the first time the IPC is analyzed (ie: equivalent to the ICV) it must be recovered within ± 5% and the precision of each measurement of the IPC must be less than 3%. Method 6010 B requires a recovery of ± 10% for both the ICV and CCV with a precision of less than 5%.

If the CCV test fails, the problem must be corrected, the instrument recalibrated and all samples since the last successful ICV (Initial Calibration Verification), CCV or check standard must be reanalyzed. Figure 1, shows the trends for

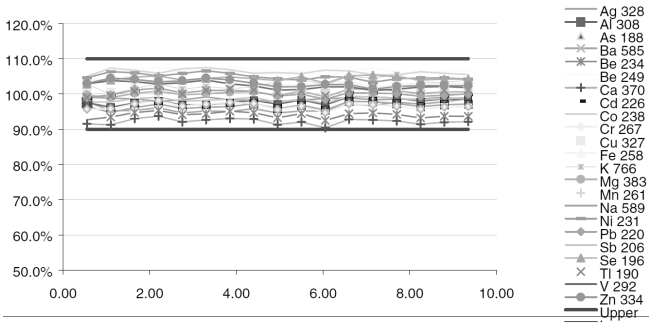

Figure 1. Percentage recoveries of Continuing Calibration Verification standards over a 10 hour period with no internal standard correction for all US EPA 22 elements at all wavelengths used. All recoveries were within the ± 10% limits.

the CCV results over a 10 hour period of continuous analysis of water samples without the use of internal standard. All CCV's fall within the US EPA acceptance criteria and the largest RSD for any element was 2%.

Interference Check Solutions (ICSA and ICSAB) and Inter-Element Corrections (IEC)

Interference Check Solutions (ICS) are used to confirm that interfering elements likely to be encountered in environmental samples do not cause incorrect measurements of analyte concentrations.

According to the US EPA criteria, inter-element interference corrections are achieved by using Inter Element Correction (IEC) factors.

These are calculated by observing the effect of known amounts of interferents on the analyte wavelengths. A table of IEC factors is generated and applied to the sample results during the analysis [4]. In ILM04.0/05.0, two solutions are analyzed - Interference Check Samples A and AB, where A contains 4 interferents only (Al, Ca, Fe and Mg) and AB contains the interferents plus 16 analytes. In the ICSA, the analytes must be within ± 2xCRDL (for elements with CRDLs ≧ 10 ug/L) and in ICSAB the analytes should be recovered within ± 20%. If the recoveries are outside these limits the "Recalibrate and Repeat With Samples" action should be conducted. For elements with CRDLs > 10 ug/L the results of the ICSA are simply reported with no test applied. The ICSA and ICSAB tests are applied at the beginning and end of the run and at a frequency of not greater than 20 samples. In Method 200.7, 17 single element, Spectral Interference Check (SIC) solutions are prepared. Concentration results at analyte wavelengths are then compared to the IDL or 3 sigma control limits of the calibration blank.

Only those failing these criteria need be tested daily, otherwise SIC testing can be conducted weekly. The results are then compared to a concentration range about the calibration blank, to determine whether SIC factors need updating. The Vista software automates the measurement, calculation and tabulation of the IEC factors. It is important to note that for accurate IEC calculations, when an internal standard correction is applied it should be applied to both the interferents and analytes. The IEC factors used in this work are not reproduced here because the factors will vary according to the analytical conditions used.

For example, use of different background correction techniques or locations will alter the appropriate IEC factor. For non EPA methods other techniques can be used to account for spectral interferences such as spectral deconvolution or the selection of alternative wavelengths.

The results for the ICSA solution analyzed at this frequency over a 10 hour period are shown in Figure 2. It can be seen that the results for Pb and Se, for example, with CRDLs of 3 and 5 µg/L respectively, are well within the allowable range for the 10 hour period.

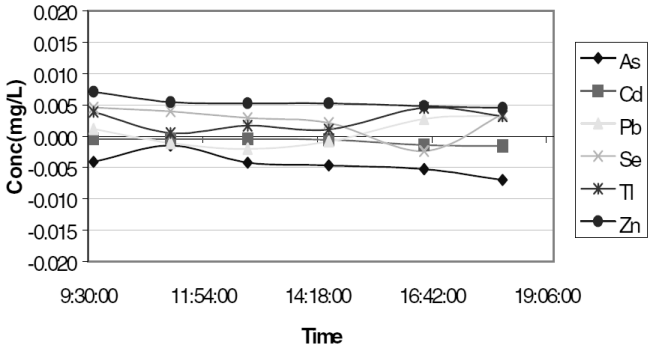

Figure 2. Concentrations of selected elements in the ICSA interferents only solution, showing that the analytes are present within the ± 2x CRDL limits for elements with CRDL < 10 ug/L over 10 hours.

Figure 3 plots the percentage recovery for the ICSAB over a 10 hour analysis period at the required frequency. Of particular interest are the results for aluminium. The Al concentration in the ICSA and ICSAB was 500 mg/L but it can be seen from Figure 3 that excellent recoveries of between 105–110% were obtained over the entire analysis period. These results indicate the excellent stability of the Vista ICP-OES at high concentrations with the axially viewed plasma.

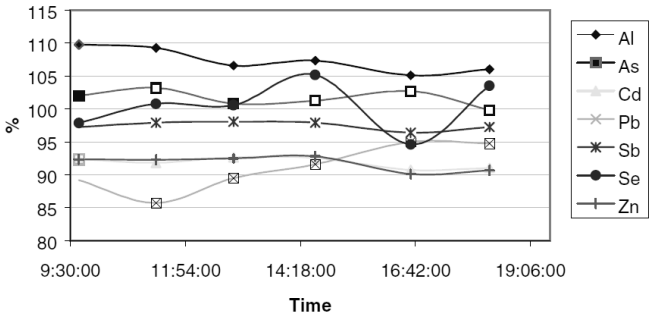

Figure 3. Percentage recoveries of selected elements in the ICSAB solution in the presence of the interferents over 10 hours are within the ± 20% limits. Note the recovery of the Al interferent which has a concentration of 500 mg/L.

Contract Required Detection Limit Test for ICP (CRI)

According to ILM04.0/05.0, to 'verify linearity near the CRDL' the laboratory is required to analyze a standard at a concentration of 'two times the CRDL or IDL whichever is greater' at the beginning and end of each sample analysis run of up to 20 samples [1]. The CRI is measured after the ICV but before the ICS. The limits to be applied to this test are not specified in the SOW [1], however the results for the analytes of interest are plotted over the 10 hour analysis period in Figure 4.

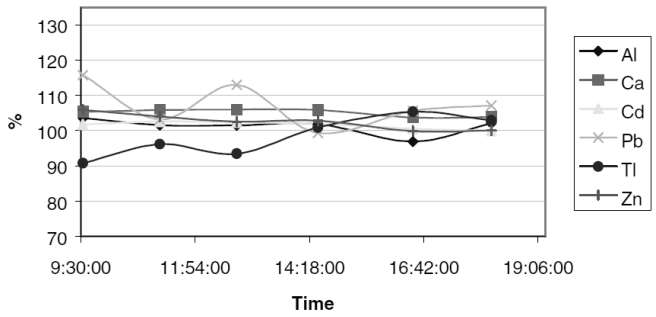

Figure 4. Percentage recoveries of the contract required detection limit test solution for ICP (CRI) for selected elements over 10 hours.

Duplicates and Spike Sample Analysis

In addition to the above tests, Duplicates and Spike Sample Analyses are required. A duplicate pair is created by processing two aliquots of the same sample through the sample preparation procedures. The Relative Percent Difference (RPD) between the original and duplicate sample is then calculated as:

$$RPD = \frac{|Sample - Duplicate\ Conc| \times 100}{(Sample + Duplicate\ Conc)/2}$$

One duplicate pair must be analyzed for each batch of 20 samples. A control limit of 20% RPD is applied to the duplicate pair for concentrations greater than 5 × CRDL. For concentrations less than this value the limit of ± CRDL is applied to the difference in the concentrations. If one result of the pair is below the 5 x CRDL limit, the ± CRDL limit is applied. If both results are less than the IDL, the RPD is not reported. The RPD of the duplicate experiment should indicate any problems due to analyte losses or contamination during the sample preparation process. Although the US EPA does not recommend an action under ILM04.0/05.0, it is generally accepted that the analysis needs to be stopped and the problem corrected before proceeding. As a result, the duplicate pair is usually analyzed at the beginning of the sample batch rather than at the end. See Table 5 for some typical duplicate results using an NIST reference as a sample.

A Spiked Sample Analysis (SSA) is performed to assess the effect of the sample matrix on analyte recoveries.

A known amount of analytes is spiked into the sample prior to digestion and the spiked sample (sometimes known as a Matrix Spike or under Method 200.7 a Lab Fortified Matrix (LFM)) is then processed through the sample preparation procedures. One SSA is required per Sample Delivery Group (batch of up to 20 samples) according to ILM04.0/05.0 and a LFM is required at a frequency of 10% according to Method 200.7. The percent recovery of the analytes is calculated and compared to the control limits 75–125% (ILM04.0/05.0) or 70–130% (Method 200.7).

If analytes are outside these limits the sample results in the SDG must be flagged and under some circumstances a post digestion spike of the affected samples may be required, see ILM04.0/05.0 Exhibit E-6.

See Table 5 for some typical SSA results.

Table 5. NIST Water Sample 1643d

Element	1643d (mg/L)	Duplicate (mg/L)	QC spike (mg/L)	1643d certified (mg/L)	% Recovery 1643d (LCS)	RPD duplicate) %	QC spike concentration	% spike recovery
Al 308.215	0.141	0.128	2.074	0.1276	111.3	9.9	2	96.6
As 188.980	0.047	0.048	2.032	0.056	96.1	2.6	2	99.2
B 249.772	0.134	0.134	0.128	0.144	103.6	0.5		
Ba 585.367	0.504	0.501	2.659	0.506	110.1	0.5	2	107.8
Be 313.042	0.011	0.011	0.062	0.0125	100.0	0.1	0.05	101.3
Ca 315.887	28.896	28.311		31.04	101.3	2.0		
Cd 226.502	0.006	0.005	0.056	0.00647	94.3	0.7	0.05	101.5
Co 228.615	0.023	0.023	0.537	0.025	103.1	0.1	0.5	102.7
Cu 327.395	0.019	0.019	0.285	0.0205	104.3	2.9	0.25	106.6
Fe 259.940	0.096	0.092	1.196	0.0912	112.1	4.7	1	110.0
4Mg 383.829	7.337	7.356		7.9889	102.3	0.3		
Mn 261.020	0.030	0.028	0.543	0.037	84.1	6.9	0.5	102.6
Mo 202.032	0.104	0.105	1.131	0.1129	103.4	1.2	1	102.7
Na 589.592	23.386	23.338	-	22.07	117.5	0.2		
Ni 231.604	0.053	0.054	0.551	0.058	103.2	0.8	0.5	99.6
Pb 220.353	0.016	0.017	0.533	0.0181	102.0	4.9	0.5	103.3
Sb 206.834	0.038	0.038	0.036	0.054	78.7	0.8		
Si 251.611	2.782	2.784	2.816	2.7	114.6	0.1		
Sr 430.544	0.249	0.249	0.243	0.294	94.2	0.0		
Tl 190.794	0.008	0.009	2.039	0.00728	136.8	7.9	2	101.5
V 311.837	0.035	0.035	0.577	0.035	112.6	0.5	0.5	108.4
Zn 206.200	0.063	0.063	0.560	0.072	97.2	0.1	0.5	99.4

Laboratory Control Sample (LCS)

The LCS is an ILM04.0/05.0 required check standard obtained from the US EPA which is processed through the same preparation procedures as the samples1. If an LCS is not available from the EPA, an ICV may be used (ILM04.0 page E-25). One LCS must be analyzed in each sample delivery group. The analytes must be recovered within limits of 80–120% of the true value for the analytes or the analysis must be terminated and the samples in that SDG redigested and reanalyzed.

In this work, a NIST Water Sample 1643d was used for the Duplicate, SSA and LCS tests. The reported values obtained in Table 5 for 1643d and the duplicate were obtained after a dilution of 9ml of sample to a final volume of 10 mL. The LCS percentage recovery, RPD of the duplicate and the percentage recovery of the SSA on NIST 1643d were all within specification.

Other Protocol Tests

The US EPA protocols also demand other tests that have not been discussed here in detail. These include Serial Dilutions, Preparation Blanks and Initial and Continuing Calibration Blanks. According to ILM0.40 [1] a serial dilution experiment consists of a five fold dilution of each sample type (water, soil). The diluted result is then compared to the original undiluted result and after allowing for dilution the results must agree within ± 10%. The analytes tested in the sample must be at concentrations of 50 times the IDL (Instrument Detection Limit) or higher. If the serial dilution is out of control for an analyte(s), the sample results associated with that serial dilution must be flagged in the laboratory reports. This may indicate that chemical or physical interferences are occuring for the sample type. A Preparation Blank is an aliquot of deionized, distilled water which has been processed through the sample preparation and analysis process [1]. The presence of contaminants in Preparation Blank is therefore indicative of contamination problems in the sample preparation process. One Preparation Blank (PBLK) is required per sample delivery group. If the absolute found concentration of the PBLK is less than or equal to the CRDL for any analyte no action is required. If any analyte in the PBLK is found at a concentration greater than the CRDL or less than the negative CRDL the lowest concentration of any sample in the SDG for that analyte must be 10 times the CRDL. Otherwise the samples must be redigested and reanalyzed and the sample concentration is not corrected for the blank value.

A typical Vista worksheet for this analysis is shown in Figure 5.

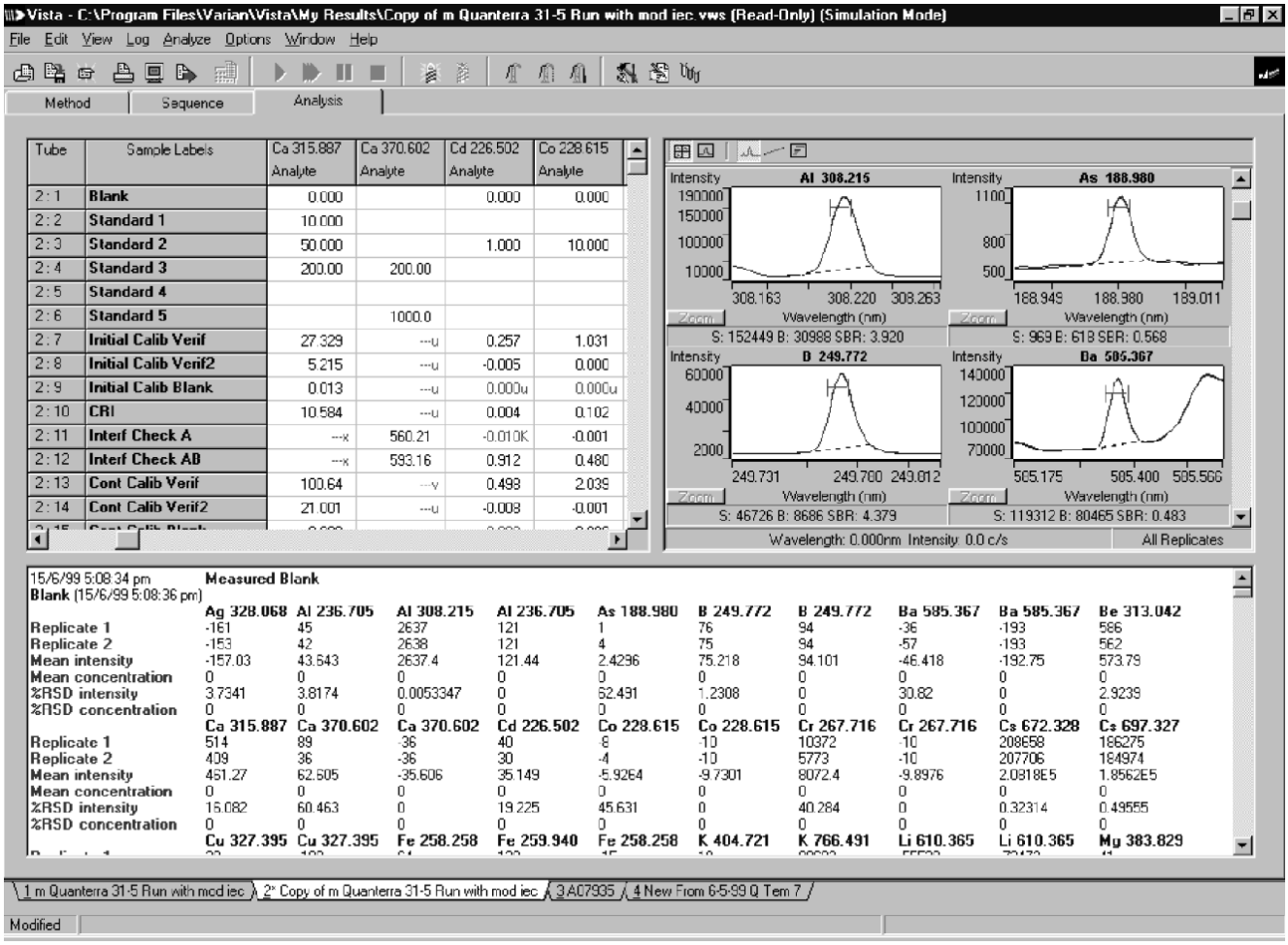

Figure 5. A typical analysis worksheet for the analysis of waters and waste waters showing two wavelengths for Ca spanning 0–1000 mg/L and the basic EPA start up sequence - calibration, ICV, ICB, CRI.

Speed of Analysis

Meeting the requirements of the US EPA protocols is time consuming due to the high overhead of quality controls required to analyze a batch of samples and the large number of variables that must be monitored to ensure compliance. The Vista simultaneous ICP-OES has been shown to meet all the rigorous US EPA specifications with a sample analysis time of 2.5 mins/sample, including a rinse time of 40 seconds per sample, two 30 second integrations plus sample delay and stabilization times. The use of dilute nitric acid and Triton X-100 in the rinse solution was found to be useful in aiding the rapid rinse out of the system.

Conclusion

In this work, a universal simultaneous ICP-OES method meeting US EPA environmental regulations has been developed for waters and waste-waters. The Agilent Vista ICP-OES provides the unique advantage of being able to achieve this task in a single analysis from an axially viewed plasma system. This avoids the time delay and costs related to repeating analyses via either other techniques or by using dual viewed ICP-OES systems.

Long term stability over 10 hours was extremely good with the general long term precision of 1% for most elements and a maximum of 2%. This was also established by noting that the CCV recoveries over the 10 hour period were all within specified limits.

Vista's MultiCal provides the benefit of combining wavelengths to cover a wider linear dynamic range from low parts per billion to high parts per million. The suitability of this approach was proved with the CRI and Linear Dynamic Range tests. The ability to choose any wavelength from the VistaChip CCD facilitates use of this extended linear dynamic range and also allows flexibility to choose wavelengths to avoid interferences. Using standard US EPA conditions, it was shown that successful compliance with the Interference Correction Standards tests could be achieved over the 10 hour period.

The Vista software provides complete automation of all the protocols identified in this article with the capability to customize these QC protocols to meet the requirements of other regulatory bodies other than the US EPA. In this work, full automatic compliance with the required US EPA protocols was possible without need for further customization. The Vista ICP-OES has been shown to meet all of the regulatory requirements in a single, fast and fully automated analysis.

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ILM04.0/05.0	Method 200.7	Method 6010B	Brief definition of function according to ILM04.0/05.0
Analytical Sample	Sample - this method does not clearly indicate counting rules	Sample - this method does not clearly indicate counting rules	Everything other than the ICV, ICB, CCV, CCB, calibration standards and calibration blank.
Sample Delivery Group (SDG)	Group of 20 samples	Not clearly stated	A unit within a sample case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer real samples within a case. Note that since sample deliveries will not include Preparation Blanks, ICSA and ICSAB and other solutions that are counted as Analytical Samples, the number of Analytical Samples for an SDG may be higher than 20.
Contract Required Detection Limit (CRDL)	No equivalent	Estimated IDLs are provided but not mandated.	The detection limits for each of the 22 elements that must be met to comply with the Statement of Work or Method.
Instrument Detection Limit (IDL)	Method detection limits (MDL) - 7 replicates of fortified reagent water at 2-3 x instrument detection limit	Method detection limits (MDL) - at 3-5 times anticipated detection limits - 7 replicates on 3 non-consecutive days 'for additional confirmation'.	The detection limit calculated by multiplying by 3 the average of the standard deviations obtained on 3 nonconsecutive days from a standard solution at a concentration of 3-5 times the instrument manufacturers suggested IDL. Seven consecutive measurements are taken to define the standard deviation under the same conditions as the proposed analytical method.
Initial Calibration Verification (ICV)	See IPC below.	ICV	Used to initially verify the validity of the calibration by measuring the recovery of analytes in this standard immediately after calibration. A second source standard.
Initial Calibration Blank (ICB)	Calibration blank	Calibration blank	A “calibration blank” that immediately follows the ICV. Usually compared to the Instrument Detection Limit (IDL).
Continuing Calibration Verification (CCV)	Initial performance check (IPC) standard - combines both ICV and CCV - first time limits are + 5%	CCV - accompanied by calibration blank - can use ICV instead - ± 10% limits plus < 5 %RSD	Used to verify the validity of the calibration on an on-going basis. This standard is measured at a frequency of every 10 'analytical samples'. Recovery limits + 10%
Continuing Calibration Blank (CCB)	Calibration blank	Calibration blank	A 'calibration blank' that immediately follows the CCV. Usually compared to the Instrument Detection Limit (IDL).
Contract Required Detection Limit Test for ICP (CRI)	No equivalent	No equivalent	A standard containing the analytes at 2 times the CRDL or IDL whichever is greater. No control limits yet applicable. Not required for Al, Ba, Ca, Fe, Mg, Na and K. Analyzed at the beginning and end of the SDG.
Interference Check Solution (ICSA)	Spectral interference check (SIC) solutions - up to 17 interferent solutions tested - test for 10% error in baseline	Interference check sample - analytes at 0.5-1.0 mg/L - interferents at 100 mg/L of Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Ti and V are shown in Table 2 of the method. - test for 20% error in baseline	Used to check the effect of interferents on the determination of the analytes. ICSA is the interferents only solution and contains Al, Ca and Mg at 500 mg/L and Fe at 200 mg/L. Analytes should be within 0 ± 2 x CRDL. Analyzed at the beginning and end of the SDG. Note the 20% error limit in the 6010B method probably refers to ± 10% since otherwise the method is exactly the same as 200.7.
Interference Check Solution (ICSAB)	See above.	See above.	Used to check the effect of interferents on the determination of the analytes. ICSAB contains both interferents and 16 selected analytes. Analytes must be recovered within ± 20%. Analyzed at the beginning and end of the SDG.
Preparation Blank (Prep Blk)	Lab reagent blank (LRB)	Method blank	Also known as a Reagent Blank. A volume of deionized distilled water processed through the sample preparation procedure. Analytes are then monitored versus the CRDL. In ILM04.0/05.0, no preparationblank correctionof samples is done. One per SDG.
No equivalent	Lab fortified blank (LFB) - an aliquot of LRB which has been spiked with analytes - one per SDG	No equivalent	
Lab Control Sample (LCS)	Quality control sample (QCS) - 3 analyses to within + 5% recovery	No equivalent	A control standard sourced from the EPA or another independent source. The LCS is put through the sample preparation process and then the recovery of the analyes is calculated and compared to ± 20% limits. One per SDG.

Continued on next page.

ILM04.0/05.0	Method 200.7	Method 6010B	Brief definition of function according to ILM04.0/05.0
Duplicate (Dup)	Laboratory duplicates (LD1 and LD2)	Matrix spiked duplicate Samples - measure 2 duplicates of a spiked sample - RPD to 20% - and spike recovery to ± 25%	A duplicate aliquot of a sample, put through the sample preparation procedure. Acts as a monitor for contamination and losses during sample preparation. The Relative Percent Difference between the duplicate and the sample is calculated and compared to ± 20% limits or CRDL limits. One per SDG. Note the Matrix Spiked Duplicate of 6010B tries to combine both the Matrix Spike and Duplicate tests into one but most ICP software is currently not designed to handle this combination.
Serial Dilution (Ser)	Dilution test	Dilution test - do for new or unusual matrices	Conduct a five fold dilution on one sample from each SDG. The calculated result after correction for dilution must agree within ± 10% of the undiluted sample result.
Spiked Sample Analysis (SSA) or Matrix Spike (MS)	Lab fortified matrix (LFM) - spike every 10 % of samples - recover to ± 30%	No equivalent (see PDSA)	A spike is added to a sample prior to the digestion or sample preparation procedures. The recovery of the spike is calculated and compared to ± 25% limits. A matrix spike is required for each SDG.
Linear Range Analysis (LRA)	Linear dynamic range (LDR) - verified annually - top standard recovered to - 10% limit - dilute all samples that are more than 90% of the LDR	LDR - as per 200.7	A standard which is analyzed quarterly to confirm the linearity of analytical calibrations. A high level standard must be recovered within 5% of the true value. This defines the upper limit of the linear dynamic range.
Post Digestion Spike - only required if the SSA fails	Analyte addition test - spike at 20-100 times the MDL - recover to ± 15% limits	Post digestion spike addition (PDSA) - do for new or unusual matrices - spike at 10-100 times the MDL - recover to ± 25% limits	Post digestion spikes are often used to assess whether the Method of Standard Additions is required. This is done separately from pre-digestion spikes because the pre¬digestion spike might be indicative of contamination picked up during the sample preparation procedure.

Typical Analysis Orders For US EPA Methods

#	Analytical sample count ILM04.0/05.0	ILM04.0/05.0	Method 200.7	6010B
2	0	Samples 20	Samples 20	Samples
1	0	Calibration blank	Calibration blank	Calibration blank
4	0	Standards	Standards*	Standards
5	0	ICV	Initial performance check (IPC)	ICV
6	0	ICB	Calibration blank	Calibration blank
7	1	CRI	Lab reagent blank method	Blank
8	2	ICSA	Lab fortified	Blank CCV
9	3	ICSAB	S1(Lab duplicate 1)	Calibration blank
10	0	CCV	S1(Lab duplicate 2)	Sample 1
11	0	CCB	S1(Lab fortified matrix)	S1 D1 (Matrix spike duplicate 1)
12	1	Prep	Blank S1 (Dilution test)	S1 D2 (Matrix spike duplicate 2)
13	2	LCS	S1 (Analyte addition test)	S1 Post digestion spike
14	3	Sample 1	Sample 2	S1 Dilution test
15	4	S1 DUPLICATE	Sample 3	Sample 2
16	5	S1 SPIKE	Sample 4	Sample 3
17	6	S1 DILUTION	IPC	Sample 4
18	7	Sample 2	Cal Blk	Sample 5
19	8	Sample 3	Sample 5	Sample 6
20	9	Sample 4	Sample 6	CCV
21	10	Sample 5	Sample 7	CCB
22	0	CCV	Sample 8	Sample 7
23	0	CCB	Sample 9	Sample 8
24	1	Sample 6	Sample 10	Sample 9
25	2	Sample 7	Sample 11	Sample 10
26	3	Sample 8	Sample 12	Sample 11
27	4	Sample 9	Sample 13	Sample 12
28	5	Sample 10	Sample 14	Sample 13
29	6	Sample 11	IPC	Sample 14
30	7	Sample 12	Cal Blk	Sample 15
31	8	Sample 13	Sample 15	Sample 16
32	9	Sample 14	S 15 (LFM)	CCV
33	10	Sample 15	Sample 16	CCB
34	0	CCV	Sample 17	Sample 17
35	0	CCB S	ample 18	Sample 18
36	1	Sample 16	Sample 19	Sample 19
37	2	Sample 17	Sample 20	Sample 20
38	3	Sample 18	IPC	CCV
39	4	Sample 19	Cal Blk	CCB
40	5	Sample 20		
41	6	CRI		
42	7	ICSA		
43	8	ICSAB		
44	0	CCV		
45	0	CCB		
	Efficiency	44.4%	51.3%	51.3%

** It is assumed that the Initial Demostration of Performance, including annual demonstration of LDR and MDLs has been done prior to analysis*

** It is assumed that the 17 Spectral Interference Check (SIC) standards have been analysed prior to the instrument calibration. Only those correction factors exceeding certain criteria need be tested daily*

** Note that a QCS (Quality Control Sample) is required by 200.7 on a quarterly basis - but since this is not a daily operation it is not indicated in the analysis list above*

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